Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil

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"Capsule": *Diammonium phosphate was the most effective treatment for immobilizing heavy metals.*

Abstract

Three chemical immobilization materials, agricultural limestone (AL), mineral rock phosphate (RP), and diammonium phosphate (DAP), were evaluated using solute transport experiments to determine their ability to reduce subsurface heavy metal transport in a smelter contaminated soil. Percent reductions in metals transported were based on comparison with cumulative totals of metal species eluted through 60 pore volumes from an untreated soil. Reductions of metal eluted from the AL treatment were 55% for Cd, 45.2% for Pb, and 21.9% for Zn. Rock phosphate mixed with soil at 60 and 180 g kg^{-1} was generally ineffective for reducing Cd, Pb, and Zn elution with <27% reduction for Cd, Pb, and Zn. Rock phosphate placed under contaminated soil as a reactive barrier (i.e. layered RP) at 180 g kg^{-1} reduced Cd 53% and Zn 24%, and was the most efficient treatment for reducing Pb (99.9%) transport. DAP treatments were superior to all other materials for reducing Cd and Zn elution with reduction >77% for Zn and >91% for Cd from the 90 g DAP kg^{-1} treatment. Increasing DAP from 10 to 90 g kg^{-1} increased total arsenic released from 0.13 to 29.5 mg kg^{-1} and total P eluted from 2.31 to 335 mg. DAP at 10 g kg^{-1} was the most effective treatment for immobilizing the combination of Cd, Pb, and Zn, with reductions of 94.6, 98.9, and 95.8%, respectively.
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1. Introduction

Mining, processing, and smelting activities have contaminated soil and water resources with heavy metals throughout the world. Geochemical weathering processes acting upon metallurgical wastes and by-products initiate the process of transporting heavy metals from contaminated areas and redistributing them to surrounding soils, streams, and groundwater ([Fuge et al., 1993; Paulson, 1997](#)). The redistribution of heavy metals by means of solute transport mechanisms can adversely affect water resources and endanger the health of surrounding ecosystems and human populations.

Soil remediation technologies based on the excavation, transport, and landfilling of metal contaminated soils and wastes are highly effective at lowering risk; however, they can also be expensive to implement. Other in-situ remediation techniques avoid transportation and landfilling costs by treating contaminants in place. In-situ chemical immobilization is a remediation technique that decreases the concentration of dissolved contaminants by sorption or precipitation. Increased sorption and decreased solubility can reduce pollutant transport and redistribution from contaminated soils, mine refuse, and smelting by-products. Furthermore, chemical immobilization treatments may also serve as reactive barriers to prevent metal seepage from recovery pits and other processing areas on active and defunct sites ([Wagner, 1994](#)). Compared with other remediation techniques, in-situ chemical immobilization is less expensive and may provide a long-term remediation

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solution through the formation of low solubility minerals and/or precipitates.

Research on chemical immobilization of heavy metals has included alkaline- and phosphate-based materials that adsorb, chelate, or complex heavy metals in soil. Alkaline materials used as chemical immobilization treatments include calcium oxides, and calcium and magnesium carbonates (Derome, 2000; Derome and Saarsalmi, 1999; Filius et al., 1998; Hooda and Alloway, 1996). Alkaline amendments reduce heavy metal solubility in soil by increasing soil pH and concomitantly increasing metal sorption to soil particles (Filius et al., 1998; McBride et al., 1997). Additionally, increased soil pH and carbonate buffering can lead to the formation of metal-carbonate precipitates, complexes, and secondary minerals (Chlopecka and Adriano, 1996; McBride, 1989; Mench et al., 1994) that decrease metal solubility and reduce metal transport.

Additions of phosphate materials or the inherent presence of sufficient levels of soil P has proven extremely effective as a chemical immobilization treatment for Pb. Ruby et al. (1994) indicated that adequate levels of soil phosphate were responsible for the formation of insoluble complexes and the reduction in potentially bioavailable Pb. Experiments involving treatment of metal contaminated soils with rock phosphates (apatite and hydroxyapatite) have shown that formation of metal-phosphate precipitates and minerals reduced heavy metal solubility. Insoluble and geochemically stable lead pyromorphites such as hydroxypyromorphite $[Pb_5(PO_4)_3OH]$ and chloropyromorphite $[Pb_5(PO_4)_3Cl]$ have been found to control Pb solubility in apatite amended contaminated soils (Chen et al., 1997; Eighmy et al., 1997; Laperche et al., 1996; Ma et al., 1993; Ma et al., 1995; Ma and Rao, 1997; Zhang and Ryan, 1999). In addition to reducing metal solubility, rock phosphate amendments are also effective at reducing metal bioavailability associated with incidental ingestion of soil by humans (Lambert et al., 1994; Zhang and Ryan, 1998) and for reducing plant bioavailability of heavy metals (Basta and Gradwohl, 1998; Chlopecka and Adriano, 1996; Laperche et al., 1997).

Other research has shown that highly soluble phosphate sources (i.e. phosphate salts) enhance the potential for formation of lead pyromorphite compared to rock phosphate (Cooper et al., 1998; Hettiarachchi et al., 1997; Ma et al., 1993; Pierzynski and Schwab, 1993). Ma and Rao (1997) suggested that P sources with higher solubility could be mixed with rock phosphate to increase the effectiveness of lead immobilization in contaminated soils. The addition of soluble phosphates from industrial sources, such as Na_2HPO_4 (Cotter-Howells and Capron, 1996) and pyrophosphate (Xie and MacKenzie, 1990), are also highly effective for forming precipitates and/or increasing sorption of Pb

and Zn. Calcium and ammonium phosphate crop fertilizers are widely available and have the potential to serve as chemical immobilization treatments. Levi-Minzi and Petruzzelli (1984) reported that diammonium phosphate $[DAP–(NH_4)_2HPO_4]$ decreased Cd solubility in soil cadmium suspensions, whereas Pierzynski and Schwab (1993) found that DAP increased metal solubility due to the acidification from nitrification. Of the soluble P sources, commercial phosphate fertilizers and sodium phosphates are the most readily available material in large quantities required for remediation of contaminated sites. However, additions of large amounts of sodium may result in soil dispersion and loss of the capability to support vegetative growth.

Most research efforts investigating chemical immobilization treatments have focused on reducing the bioavailability (i.e. plants, human gastrointestinal), solubility, or extractability (i.e. sequential extractions) of metals. Additional information is needed on the effect of chemical treatments for reducing the mobility and transport of Cd, Pb, and Zn. The objective of this study was to compare the ability of agricultural limestone, rock phosphate, and diammonium phosphate treatments to reduce heavy metal transport in a smelter contaminated soil.

2. Materials and methods

2.1. Soil characterization

Surface soil (<20 cm) with elevated residual concentrations of Cd, Pb, Zn, and As (Table 1) was collected from an inoperative smelter site in Northeastern Oklahoma. Soil was air-dried and sieved (<2 mm) prior to use. Collected soils had been treated with coarse limestone approximately 4 months prior to the date of collection. Soil pH (1:1, soil:water) determined by combination electrode was 6.8. Particle size analysis determined using the hydrometer method (Gee and Bauder, 1986) indicated the soil was a sandy loam (USDA classification) with 67% sand, 29% silt, and 4% clay. Total metal contamination in the soil was determined by X-ray fluorescence spectroscopy (XRF) is also reported in Table 1. Pressed powder pellets were prepared from ground soil samples (<100 mesh) followed by direct elemental determination of the sample (Karathanasis and Hajek, 1996). The contaminated soil was also tested to determine its hazardous waste disposal status using the Toxicity Characteristic Leaching Procedure (TCLP, SW-846 Method 1311) (US EPA, 1986). Furthermore, the soil was extracted with 0.5M $Ca(NO_3)_2$ at a 1:20 soil:solution ratio for 16 h to estimate potential metal bioavailability (Basta and Gradwohl, 2000).

Table 1
Total content, TCLP extractable, and 0.5 M Ca(NO$_3$)$_2$ extractable Cd, Pb, As, and Zn for the smelter-contaminated soil

Element	Total content[a] mg kg^{-1}	TCLP Extractable		0.5M Ca(NO$_3$)$_2$ Extractable mg kg^{-1}
		mg l^{-1}	Reg. limit[b]	
Cd	1090	39.9±1.59	1.0	155.7±4.44
Pb	5150	21.0±0.58	5.0	12.3±0.43
As	152	0.03±0.002	5.0	0.25±0.02
Zn	69,200	1171±32	NA	585.5±17.8

[a] Total content determined by X-ray fluorescence.
[b] Regulatory limit in mg l^{-1} specified by US EPA Method 1311 (US EPA, 1986).

2.2. Chemical immobilization treatments

Three chemical treatment materials were evaluated for reducing the solubility and transport of Cd, Pb, and Zn: agricultural limestone (AL) (104% effective calcium carbonate equivalent (ECCE) as CaCO$_3$), mineral rock phosphate (RP) (12.4% P- carbonated fluorapatite North Carolina source- 40 mesh), and reagent grade diammonium phosphate (DAP 23% P) [(NH$_4$)$_2$HPO$_4$]. Treatments were: check soil with no chemicals added, 10 g DAP kg^{-1}, 90 g DAP kg^{-1}, 60 g RP kg^{-1}, 180 g RP kg^{-1}, and 170 g AL kg^{-1} mixed thoroughly with the soil. An additional treatment included 180 g RP kg^{-1} layered in the transport column to simulate the potential use of RP as a reactive barrier.

Phosphate amendments were based on providing a specific P/total metal (M$_{total}$) molar ratios. Total metal, for the purpose of the immobilization treatments, was defined as the sum of total Cd, Pb, and Zn determined by XRF. This treatment structure was chosen with the intent to immobilize the total concentrations of the three metal species in the smelter-contaminated soil. Previous research has used the ratio of 3/5 P/M$_{total}$ as the basis of hydroxyapatite and apatite treatments to lead-contaminated soils (Laperche et al., 1996; Ma et al., 1993; Zhang et al., 1998; Zhang and Ryan, 1999). This ratio corresponds to the stoichiometric P/Pb ratio for chloropyromorphite [Pb$_5$(PO$_4$)$_3$Cl]. The 180 g RP kg^{-1} treatment corresponds to an approximate 3/5 P/M$_{total}$ ratio, and the 60 g RP kg^{-1} to a 1/5 P/M$_{total}$ ratio. These RP treatments were mixed thoroughly with the soil prior to repacking in the transport columns. In addition to investigating mixed RP treatments, a layered treatment of 180 g RP kg^{-1} was also included to simulate a reactive chemical barrier. For this treatment, the entire amount of RP equivalent to 180 g RP kg^{-1} was layered on one end of the column and the remaining volume of the column packed with contaminated soil. The layer was positioned between the contaminated soil and the outflow boundary of the repacked soil column. Due to the low inherent solubility of RP, the total amount of phosphate applied with the RP source will not congruently dissolve and produce high solution concentrations of phosphorus. In contrast to the low solubility RP source, using the highly water-soluble (99.9% water soluble) DAP source in a 3/5 P/M$_{total}$ molar ratio (90 g DAP kg^{-1}) results in very high concentrations of soluble phosphate (20700 mg P kg^{-1}). Therefore the lower treatment of 10 g DAP kg^{-1} (2300 mg P kg^{-1}) which corresponds to a 1/15 P/M$_{total}$ ratio was also investigated. The agricultural limestone treatment was based on the formation of metal-carbonate precipitates, with the general formula [MCO$_3$], where M = M$_{total}$ as previously described. The actual rate of 170 g AL kg^{-1} was 1.5 times the stoichiometric amount needed to convert M$_{total}$ to metal-carbonate precipitates.

2.3. Solute transport

Chemical immobilization treatments were evaluated using solute transport experiments with repacked soil columns similar to methods described by Selim and Amacher (1996). Column dimensions were 4 cm i.d. by 7.5 or 10 cm length. Teflon filters (0.45 μm, Micron Separations, Inc., Westboro, MA) were placed between the soil matrix and end caps on each end of the column to prevent loss of fines from the soil column. An additional filter of the same type was placed between the soil matrix and each side of the RP layer on the 180 g RP kg^{-1} layered treatment. Soils were saturated with type 1 reagent grade water (>18.0 MΩ·cm at 25 °C) (ASTM, 1992) with continuous upward flow using a piston pump (Fluid Metering, Inc., Syosset, New York) until saturation, when flow was stopped and the column allowed to equilibrate for 48 hours prior to miscible displacement. Eighmy et al. (1997) indicated that 24 h was sufficient for pseudo-equilibrium and solid phase precipitation of metal compounds to occur with additions of soluble phosphate to combustion residues. Our preliminary studies showed that a steady state within the column was obtained after 24 h of pre-equilibration; however, we selected a pre-equilibration period of 48 hours for added insurance of an equilibrated system. After the equilibration period, a saturated upward flow regime was resumed and soil solution fractions were collected with a fraction collector (ISCO Inc., Lincoln, NB) through 60 pore volumes. Column effluent was passed through Teflon tubing and an in-line 0.45 μm filter before collection into glass test tubes. Sample effluent pH was immediately analyzed after collection by combination electrode. Effluent aliquots were analyzed for solution phosphate using the modified ascorbic acid method (Murphy and Riley, 1962). Effluent was then acidified with trace metal grade HNO$_3$ to pH < 2 (APHA, 1992) prior to metal analysis (Al, As, Ba, Ca, Cd, Cr, Cu, K, Fe, Mg, Mn, Na, Ni, Pb, Zn) by Inductively Coupled Plasma Atomic Emission Spectrometry

(ICP-AES). Metal concentration measured in eluted fractions was normalized to concentrations per 100 g of soil for comparison of treatments. Elution curves for As, Cd, Pb, P, and Zn were plotted for each column experiment. Numeric integration of metal mass eluted (through 60 pore volumes) per mass of soil was calculated and Darcy flux (q), and soil bulk density (ρ_b) were determined.

Following each metal elution experiment, 50 mg Br L^{-1} solution was introduced as a conservative tracer to investigate the possibility of transport related non-equilibrium. The tracer solution was introduced as a continuous flow until complete breakthrough was obtained. Collected effluent fractions were analyzed for Br^- by ion chromatography. Bromide tracer breakthrough curves were plotted and fit using the model COLUMN 1.4 (Brown et al., 1997) to examine the flow regime and determine the potential for transport related non-equilibrium.

Chemical analyses were performed using calibration curves determined from standards prepared from certified stock solutions. Sample blanks were analyzed to determine and correct for any matrix effects. Trace metal control standards were used to assess instrument precision and accuracy. Limits of detection (LOD) were determined from the summation of three standard deviations (3σ) of the instrument response for seven repeated analyses of a sample blank solution. Practical quantitative limits (PQL) of detection were set at ten times the LOD (APHA, 1992). Solution concentrations below the PQL were assigned the value of zero in data analysis.

3. Results and discussion

3.1. Soil properties and contaminants

Total Cd, Pb, and Zn in the soil are well above background soil concentrations (Holmgren et al., 1993) indicating a highly contaminated soil (Table 1). TCLP extractable Cd and Pb exceed regulatory levels indicating the soil qualifies as a hazardous material that requires remediation and disposal in a hazardous waste facility (Table 1). The high amounts of Cd, Pb, and Zn extracted with 0.5M $Ca(NO_3)_2$ indicate a large portion of the total heavy metals in the soil is potentially bioavailable (Table 1) (Basta and Gradwohl, 2000). Total elemental content in g kg^{-1} (in parentheses) were: Si (193), Al (38), Ca (24), Mg (2.5), K (6.1), Fe (47), Mn (1.9), Ti (3.2), P (0.39), and Cr (0.27). As indicated by the Si–Fe ratio, the collected material exhibits chemical properties of soil and not an iron-based smelting waste. Saturated paste extractions were used to determine soluble anions and EC. Soluble anions in mg l^{-1} (in parenthesis) were: Cl (26.6), SO_4 (1560), and NO_3 (21.7). Soil EC was 2.15 dS m^{-1}.

The effect of soil treatment on soil pH and TCLP-extractable Cd and Pb is shown in Table 2. Diammonium phosphate treatments showed the greatest

reduction in TCLP Pb and Cd but still exceeded the US EPA regulatory levels. The TCLP method, a diluted acetic acid extraction of waste, was developed to estimate the potential of a contaminant to leach from a landfill. However, this method is not quantitative and cannot be used to describe long-term environmental fate (e.g. leaching). Contaminant transport models are the best methods used to describe the long-term environmental threat of soil contaminants leaching to groundwater not TCLP. The effect of soil treatments on transport parameters is discussed in the following section.

3.2. Contaminant transport

Solution pH was 7.0±0.2 throughout the duration of all column elution experiments. Solution calcium eluted throughout the duration of all experiments exceeded 0.005 M Ca (200 mg Ca l^{-1}) indicating a well-buffered system from the previous limestone amendments to the soil. Because soil solutions were well buffered with respect to Ca, the exclusion of additional background electrolytes from the eluting solution likely had no adverse effect on soil structure or aggregate stability during leaching. The experiment values for bulk density, Darcy flux, and pore volume are given in Table 3. Soil bulk densities (ρ_B) in the repacked columns ranged between 1.26 and 1.38 g cm^{-3} and Darcy flux between 1.70–4.88 cm h^{-1}. The degree of variability in Darcy flux for repacked columns is typical of studies using repacked columns.

Bromide breakthrough curves for all columns were sigmoid shaped and showed no apparent tailing, indicating homogenous packing and well-satisfied boundary conditions. The Br breakthrough curves showed behavior representative of a conservative tracer in porous media and conformed to the assumption of local equilibrium with r^2 values above 0.99 for all fitted curves (McGowen, 2000). These results indicate that transport-related non-equilibrium, such as that caused by preferential flow or dual porosity media, was not a factor in any of the experiments.

The ability of treatments to reduce Cd eluted (Fig. 1), eluted Pb (Fig. 2), and eluted Zn (Fig. 3) in the contaminated soil followed the trend DAP > AL, RP. Increasing the amount of treatment applied had little effect on eluted Cd, Pb, or Zn. Similar Cd, Pb, or Zn elution curves were obtained for 60 and 180 g kg^{-1} RP treatments. Similar Cd, Pb, or Zn elution curves were obtained between 10 and 90 g kg^{-1} DAP treatments. Specific discussions of treatment effects on metal elution are detailed in the following sections.

3.3. Rock phosphate treatments

The effects of RP treatments on the elution of Cd (Fig. 1), Pb (Fig. 2), and Zn (Fig. 3) from the

Table 2
Effect of soil amendment on soil pH and TCLP extractable Pb and Cd

Amendment	Treatment[a] g kg^{-1}	Soil pH	TCLP Pb[b] mg l^{-1}	TCLP Cd[b] mg l^{-1}
Untreated control	–	6.97	44.8	49.3
Rock phosphate	60	7.10	41.9	44.6
Rock phosphate	180 L	6.84	46.3	49.7
Rock phosphate	180 M	7.11	31.3	39.9
Limestone	170	7.30	43.0	44.9
Diammonium phosphate	10	8.02	11.0	23.9
Diammonium phosphate	90	7.45	5.11	0.53

[a] Layered treatment (L), Mixed treatment (M).
[b] U.S. EPA regulatory limits are 5.0 mg l^{-1} for Pb and 1.0 mg l^{-1} for Cd.

Table 3
Summary of transport parameters from untreated and treated soils

Amendment	Treatment g kg^{-1}	Length cm	Flux cm hr^{-1}	Bulk density g cm^{-3}	Pore volume mL
Untreated control	–	7.5	1.70	1.31	39.4
Rock phosphate	60	7.5	2.06	1.34	38.1
Rock phosphate	180 L[a]	10	4.88	1.36	49.9
Rock phosphate	180 M[b]	7.5	2.46	1.38	36.5
Limestone	170	10	4.72	1.36	49.7
Diammonium phosphate	10	7.5	2.43	1.29	40.1
Diammonium phosphate	90	10	4.84	1.26	5.4

[a] Layered treatment (L).
[b] Mixed treatment (M).

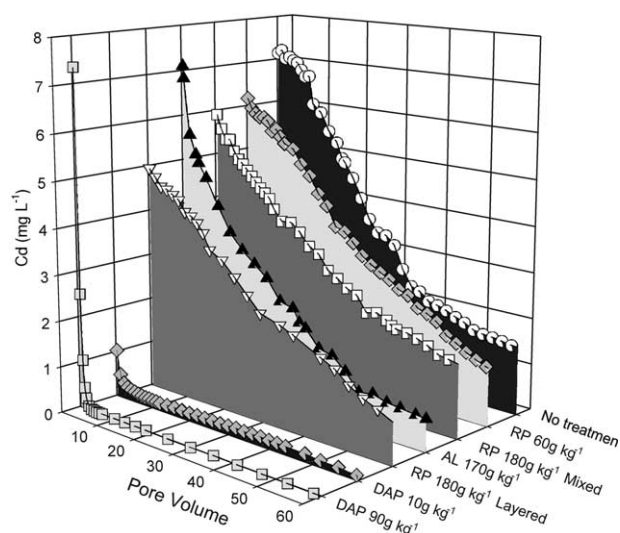Fig. 1. Cadmium elution curves for untreated and soils treated with diammonium phosphate (DAP), agricultural limestone (AL), or rock phosphate (RP).
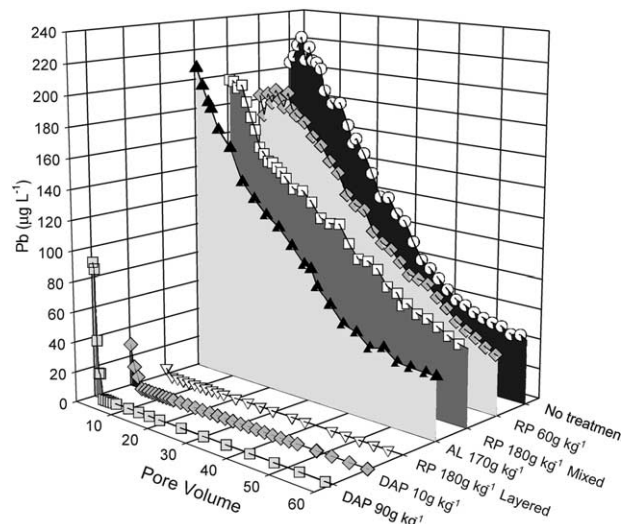

Fig. 2. Lead elution curves for untreated and soils treated with diammonium phosphate (DAP), agricultural limestone (AL), or rock phosphate (RP).

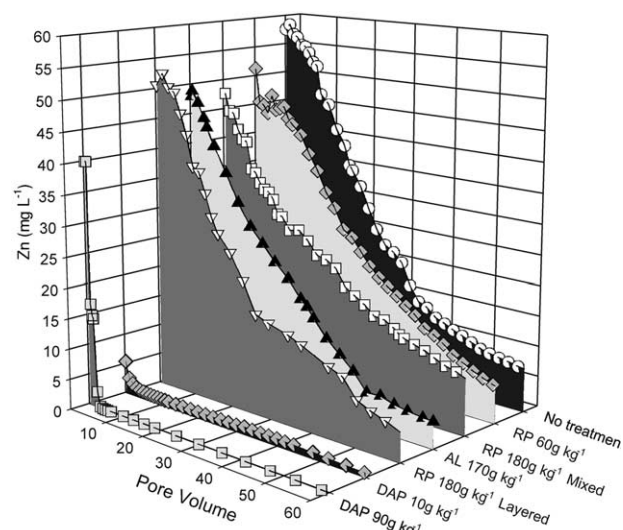
Fig. 3. Zinc elution curves for untreated and soils treated with diammonium phosphate (DAP), agricultural limestone (AL), or rock phosphate (RP).

smelter-contaminated soils through 60 pore volumes of elution were determined. Layered RP at 180 g kg^{-1} showed 99.9% reduction in Pb eluted compared with the untreated check, but was less effective in reduction eluted Cd (53%) and Zn (24%) (Table 4). Mixed RP treatments reduced Cd, Pb, and Zn leached from the contaminated soil, but reductions were <27% of total metals eluted from the untreated soil for the 180 g RP

kg^{-1} treatment and <15% of total metals eluted for the 60 g RP kg^{-1} treatment (Table 4). Phosphorus was not detected (PQL = 0.02 mg P L^{-1}) in effluent from any of the RP treated soils. Overall, metal elution curves for all RP treatments, with the exception of the 180 g RP kg^{-1} layered treatment and Pb elution, were of similar shape of the untreated soil metal elution curve but at slightly lower concentrations (Figs. 1–3). The improved reduction efficiency for Cd and Pb by the layered RP treatment compared with the mixed RP treatments could be due to greater time of contact between dissolved metal contaminants and rock phosphate surfaces. Results suggest there was greater contact time between metals and rock phosphate surfaces for layered RP compared

Table 4
Cumulative amount of As, Cd, Pb, and Zn collected per kg of smelter-contaminated soil through 60 pore volumes of elution and the percent reduction (%R) of metal species eluted compared with the untreated control (in parentheses). Phosphorus eluted through 60 pore volumes of elution is reported as mass per column

Amendment	Treatment g kg^{-1}	As mg kg^{-1}	Cd mg kg^{-1} (%R)	Pb μg kg^{-1} (%R)	Zn mg kg^{-1} (%R)	P mg column^{-1}
Untreated control	–	0.0	14.9 (0.0)	460 (0.0)	108 (0.0)	ND
Rock phosphate	60	0.0	12.7 (14.8)	418 (9.1)	94.1 (12.9)	ND
Rock phosphate	180 L[a]	0.0	7.0 (53.0)	0.5 (99.9)	81.6 (24.4)	ND
Rock phosphate	180 M[b]	0.0	10.9 (26.8)	376 (18.3)	79.3 (26.6)	ND
Agricultural limestone	170	0.0	6.7 (55.0)	252 (45.2)	84.4 (21.9)	ND
Diammonium phosphate	10	0.13	0.8 (94.6)	5.2 (98.9)	4.5 (95.8)	2.31
Diammonium phosphate	90	29.5	1.2 (91.9)	44.7 (90.3)	24.7 (77.1)	335

ND = Not detected.
[a] Layered treatment (L).
[b] Mixed treatment (M).

to mixed RP. The concentration of the reactive surface area of RP within the layer apparently increased the kinetic rate of mineral sorption and/or precipitation of metals in solution. This effect could be due to the concentration of reactive mineral surface area or to the formation of a chemical microenvironment present within the RP layer that provided for improved immobilization of Pb and Cd compared with mixed RP treatments.

3.4. Limestone treatments

The agricultural limestone treatment reduced Cd eluted 55%, reduced Pb eluted 45.2%, and reduced Zn eluted 21.9% compared to the respective totals for each species eluted from the untreated soil (Table 4). The average effluent pH from the AL treatment was 7.4 compared with 6.8 for the untreated soil. This effluent pH favors the formation of heavy metal carbonates. Total dissolved metal concentration in equilibrium with solution at pH 7.4 would be 5.8 mg Zn L^{-1}(aq) for ZnCO$_3$, 0.02 mg Pb L^{-1}(aq) for PbCO$_3$, and 0.40 mg Cd L^{-1}(aq) for CdCO$_3$ (Table 5). Our eluted metal concentrations were 12-fold greater for Zn, 11-fold greater for Pb, and 20-fold greater for Cd; therefore, the equilibration time of 48 h may not have may not have been adequate for complete metal immobilization as metal-carbonate precipitates (i.e. kinetic limiting). Longer equilibration times prior to re-initiation of the leaching process may have provided improved efficiency of the AL treatment for reducing metal elution from the contaminated soil.

Table 5
Thermodynamic dissolution constants (i.e. solubility product constants, K$_{sp}$) of for respective Pb, Cd, and Zn mineral dissolution reactions

Mineral	Equilibrium Reaction	Log K$_{sp}$	Source
Octavite	CdCO$_3$ = Cd^{2+} + CO$_3^{2-}$	−11.3	[a]
Cd(OH)$_2$	Cd(OH)$_2$ = Cd^{2+} + 2 OH$^-$	−14.7	[a]
Cadmium phosphate	Cd$_3$(PO$_4$)$_2$ = 3 Cd^{2+} + 2 PO$_4^{3-}$	−38.1	[a]
Soil cadmium	Soil-Cd = Cd^{2+}	−7.00	[b]
Anglesite	PbSO$_4$ = Pb^{2+} + SO$_4^{2-}$	−7.79	[b]
Lead phosphate	PbHPO$_4$ = Pb^{2+} + HPO$_4^{2-}$	−11.43	[c]
Cerrusite	PbCO$_3$ = Pb^{2+} + CO$_3^{2-}$	−12.8	[d]
Lead hydroxypyromorphite	Pb$_5$(PO$_4$)$_3$OH = 5 Pb^{2+} + 3 PO$_4^{3-}$ + OH$^-$	−76.8	[c]
Lead chloropyromorphite	Pb$_5$(PO$_4$)$_3$Cl = 5 Pb^{2+} + 3 PO$_4^{3-}$ + Cl$^-$	−84.4	[e]
Smithsonite (calamine)	ZnCO$_3$ = Zn^{2+} + CO$_3^{2-}$	−9.9	[f]
Zincite	ZnO + 2 H$^+$ = Zn^{2+} + H$_2$O	11.16	[b]
Hopeite	Zn$_3$(PO$_4$)$_2 \bullet$4H$_2$O = 3 Zn^{2+} + 2 PO$_4^{3-}$ + 4H$_2$O	−35.4	[g]
Zinc pyromorphite	Zn$_5$(PO$_4$)$_3$OH = 5 Zn^{2+} + 3 PO$_4^{3-}$ + OH$^-$	−63.1	[f]

[a] Jurinak and Santillian-Medrano, 1974.
[b] Lindsay, 1979, 2001.
[c] Nriagu, 1972.
[d] Santillian-Medrano and Jurinak, 1975.
[e] Nriagu, 1973.
[f] Nriagu, 1984.
[g] Kuo, 1986.

3.5. Diammonium phosphate treatments

Both DAP treatments extensively decreased the amounts of Cd eluted from the contaminated soil (Fig. 1). For the 90 g DAP kg^{-1} treatment, solution Cd fell below the instrument PQL (6 μg l^{-1}) at 4 pore volumes and remained below measurable limits through 60 pore volumes. Compared with the untreated soil, a reduction of 94.6 and 91.9% of the total Cd eluted was obtained with the 10 and 90 g DAP kg^{-1} treatments, respectively (Table 4). DAP also decreased the amounts of Pb eluted (Fig. 2) with only 1.1% of the total eluted (99% reduction) compared with the control soil for the 10 g DAP kg^{-1} treatment (Table 4). Furthermore, eluted Pb in solution was reduced below the instrument PQL (70 μg l^{-1}) after 2.5 pore volumes for the 90 g DAP kg^{-1} and after 3.2 pore volumes for the 10 g DAP kg^{-1} treatments. Eluted Zn was also reduced by addition of DAP (Fig. 3), with Zn in solution falling below the PQL (15 μg l^{-1}) after 4.6 pore volumes for the 90 g DAP kg^{-1} treatment. However, total reduction of Zn based on the untreated soil was far greater (95.8%) for the 10 g DAP kg^{-1} treatment than for the 90 g DAP kg^{-1} treatment (77.1%).

Elution curves of Cd, Pb, and Zn from the 90 g DAP kg^{-1} treatment all exhibited higher initial concentrations than the 10 g DAP kg^{-1} treatment, but then quickly decreased to solution concentrations below instrument detection. For the 90 g DAP kg^{-1} treatment, solution collected from the first 5–7 pore volumes of elution was dark colored at early times and faded to clear after approximately 10 pore volumes. The coloration of effluent fractions was unique to this treatment and may have indicated the formation of humic compounds or metal-organic complexes. Phosphate compounds have long been used in extraction of soil organic matter for characterization (Swift, 1996). The high amounts of phosphate likely extracted soluble organic matter and possibly mobile metal–organic complexes. In addition to the potential of complex formation, the Darcy flux for the 90 g DAP kg^{-1} treatment was 2-times greater than for the 10 g DAP kg^{-1} treatment. This higher flux may have further contributed to the chemical disequilibration in the system at early elution times and increased the solution concentration of heavy metals available for transport.

Application of DAP at 90 g kg^{-1} released large amounts of As from the contaminated soil (Fig. 4). Increasing DAP from 10 to 90 g kg^{-1} elevated the total As eluted from 0.13 to 29.5 mg kg^{-1} over 60 pore volumes (Table 4), with As concentrations in solution as high as 147 mg As l^{-1}. Phosphate additions increased As elution apparently by phosphate–arsenate ligand exchange. Peryea and Kammereck (1997) and Peryea (1991) reported similar phosphate induced release and transport of As when P was added to orchard soils spiked or contaminated with lead arsenate.

3.6. Phosphate elution

Large additions of P to the contaminated soil may increase the risk of eutrophication to phosphate-limited surface water bodies. Phosphorus elution curves for the DAP amended column experiments are shown in Fig. 5. As P application increased, the mass of P eluted from the treated soil columns increased. Total phosphorus eluted from the DAP treatments through 60 pore volumes was 2.31 mg for the 10 mg DAP kg^{-1} treatment and 335 mg for the 90 mg DAP kg^{-1} (Table 3). The summation of total P eluted from the 10 mg DAP kg^{-1} treatment corresponds to <1% of the total P added to the system; however, P eluted from the 90 mg DAP kg^{-1} represents 10.5% of the total P added. The low percentage of total P eluted from the 10 mg DAP kg^{-1} treatment indicates an adequate pre-equilibration period for sorption and/or precipitation to occur. As previously indicated, excessive As was released with the 90 mg DAP kg^{-1} treatment that may have contributed to chemical non-equilibrium of heavy metals with this treatment. Additions of soluble phosphate >10 mg DAP kg^{-1} (>2300 mg P kg^{-1}) may have limited potential for improving reduction of eluted heavy metals from this soil and will likely increase eluted P and As. Soluble phosphate was not detected in the RP and AL treated experiments.

3.7. Effects of chemical treatments on soil pH

Ammonium-based fertilizers can result in soil acidification (Sposito, 1989). Soil acidification from diammonium phosphate amendments would increase metal solubility and mobility in soils. To investigate the effect of chemical treatments on soil acidification, amended soils were incubated at 0.22% volumetric water content at 30 °C for 6 months. Soil pH was monitored periodically using a 1:1 soil:water ratio and a combination pH electrode. For the DAP amended soils, soil pH values decreased from 7.1 to 6.5 after 2 months and then remained constant for two more months of investigation. The buffering of the soil from previous application of limestone added to the soil (in the field and prior to collection) may have prevented a further decrease in pH. It is likely that without previous lime application to the soil that the pH may have further decreased to critical levels where metal solubility increases. The use of liming materials with the application of soluble ammonium phosphates may be required to prevent decreases in soil pH and concomitant increases in metal solubility over time. Other researchers have used liming materials along with soluble phosphate treatments to buffer against decreases in pH (Brown et al., 1999; Hettiarachchi et al.,
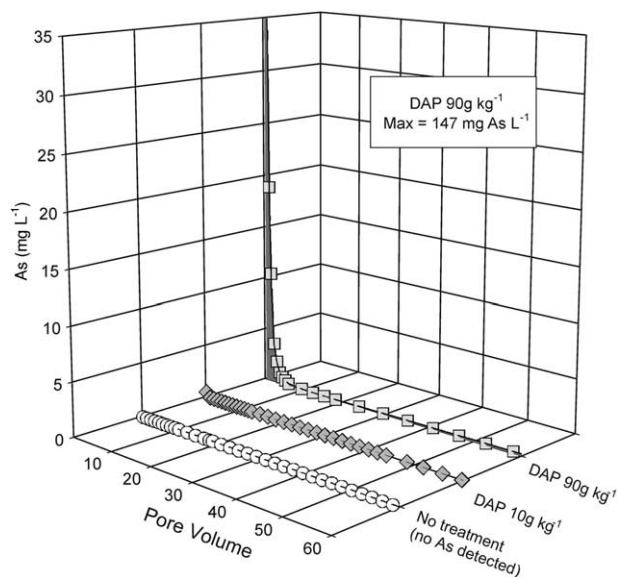
Fig. 4. Arsenic elution curves for untreated and soils treated with diammonium phosphate (DAP), agricultural limestone (AL), or rock phosphate (RP).
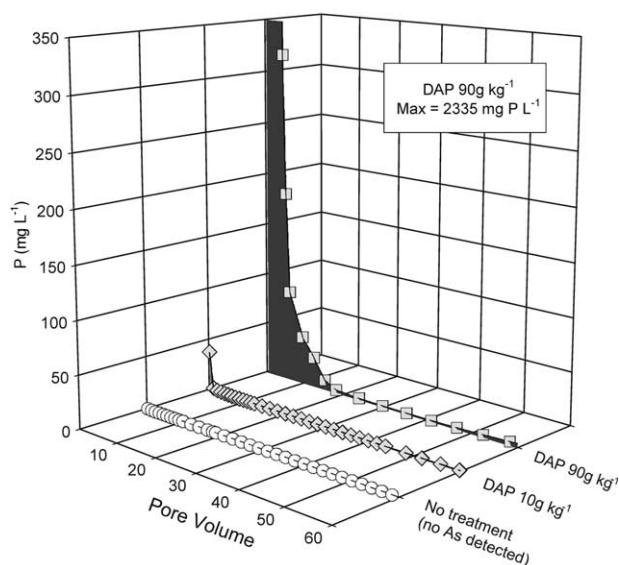

Fig. 5. Phosphorus elution curves for untreated and DAP amended soils.

1997, 1999) and many of the rock phosphate sources are carbonated forms of apatite that have some liming material value. As expected, change in soil pH with the AL and RP treatments was negligible with pH values in the neutral (6.9–7.1) range after the incubation period.

3.8. Probable mineral solid phases and metal solubility

Chemical immobilization treatments may decrease metal solubility through the formation of metal-phosphate precipitates and increase long-term stability by forming less soluble and more stable metal-phosphate

minerals (Mench et al., 1998). Long-term geochemical stability of the solid phases formed by chemical immobilization should be evaluated to determine the potential long-term effectiveness of such treatments. Decreases in metal contaminant elution due to chemical immobilization is often due to the formation of metal phosphate precipitates or minerals (McGowen and Basta, 2001). Research conducted on the treated soils used in the column study described in this manuscript showed cadmium phosphate [e.g. $Cd_3(PO_4)_2$] or octavite (e.g. $CdCO_3$) may control Cd solubility in soils before immobilization treatments (McGowen et al., 2001). Cadmium phosphate was the most probable solid phase, based on use of geochemical computer speciation modeling, after DAP treatment. Eluted Cd concentrations from limestone treated soil exceeded Cd concentration in equilibrium with $CdCO_3$. The solubility of Cd of $Cd_3(PO_4)_2 < CdCO_3$ at soil pH of DAP- and limestone-treated soils of the current study (McGowen et al., 2001) supports the conclusion that DAP would still be a more effective treatment than limestone in reducing Cd elution. Other work has shown that $Cd_3(PO_4)_2$ can control Cd solubility in phosphate sufficient soils or soils amended with phosphate (Santillian-Medrano and Jurinak, 1975; Street et al., 1977).

Research conducted on the treated soils used in the column study described in this manuscript showed angelsite (e.g. $PbSO_4$) or lead phosphates may control Pb solubility in soils before immobilization treatments (McGowen et al., 2001). Lead hydroxypyromorphite was the most probable solid phase, based on use of geochemical computer speciation modeling, after DAP treatment. Lead hydroxypyromorphite has been recognized as a mineral controlling Pb solubility in many soils amended with phosphate materials (Santillian-Medrano and Jurinak, 1975) and its formation in phosphate-treated contaminated soil has been confirmed by XRD and SEM-EDX (Cotter-Howells and Capron, 1996; Laperche et al., 1996; Laperche et al., 1997; Ma et al., 1993; Ruby et al., 1994). Similar to Cd findings, eluted Pb concentrations from limestone treated soil exceeded Pb concentration in equilibrium with $PbCO_3$. The solubility of Pb hydroxypyromorphite $<< PbCO_3$ at soil pH of DAP- and limestone-treated soils of the current study (McGowen et al., 2001) supports the conclusion that DAP would still be a more effective treatment than limestone in reducing Pb elution.

Results comparing phosphate- and carbonate-based immobilization treatments for Cd and Pb are similar to Zn. Treatment of contaminated soils with DAP were consistent with formation of zinc phosphate minerals (McGowen et al., 2001). Similar to Cd and Pb findings, eluted metal concentrations from limestone treated soil exceeded metal concentration in equilibrium with their respective carbonate minerals. The solubility of Zn phosphates $<< ZnCO_3$ at soil

pH of DAP- and limestone-treated soils of the current study (McGowen et al., 2001) supports the conclusion that DAP would still be a more effective treatment than limestone in reducing Zn elution.

4. Summary and conclusions

Of the treatments investigated, 10 g DAP kg^{-1} was the most effective for immobilizing heavy metals eluted from the contaminated soil with reductions of 94.6% of Cd, 98.9% of Pb, and 95.8% of Zn eluted when compared with the untreated soil. Application of DAP caused As release via ligand exchange from the contaminated soil at applications >10 g DAP kg^{-1}. Increasing DAP amendment to the contaminated soil from 10 to 90 g kg^{-1} increased the total As eluted from 0.13 to 29.5 mg kg^{-1} over 60 pore volumes. Total phosphorus eluted from the DAP treatments (60 pore volumes) was 2.31 mg (<1% of the total added) for the 10 mg DAP kg^{-1} treatment and 335 mg (10.5% of the total added) for the 90 mg DAP kg^{-1} treatment. Layered RP at 180 g kg^{-1} was the most effective treatment for reducing Pb transport with a 99.9% reduction over the untreated control; however, DAP treatments outperformed this treatment for Cd and Zn elution. Mixed RP at both treatments investigated was mostly ineffective in reducing Cd, Pb, and Zn elution from the contaminated soil. Limestone, although moderately effective for reducing Cd (55%) and Pb (45.2%) over the untreated check, was a poor performer for removing Zn (21.9%) from solution.

Chemical immobilization of heavy metals using DAP provided the most effective method of reducing metal transport. DAP treatments not only removed large amounts of Pb from solution, but were also highly effective at reducing Cd and Zn solubility and transport. Application schemes with DAP must be carefully planned to reduce As release and P elution, and co-application of liming materials with DAP may be necessary to offset potential soil acidification.

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